

NOTE

Synthesis of Polymers with Alkylaminopyridine Functions as a Supernucleophilic Reagent

YAKAI FENG,^{1,4} LI ZHANG,² JITAO HUANG,³ JINGWU SUN⁴

¹ Textile Chemie und Makromolculare Chemie, RWTH Aachen, 52062, Aachen, Germany

² Institute for Molecular Biology, Nankai University, Tianjin 300071, Tianjin, People's Republic of China

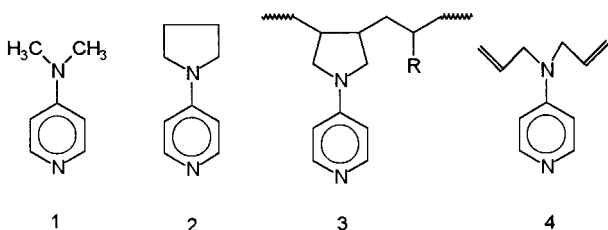
³ Department of Chemical Engineering, Tianjin Institute of Technology, Tianjin 300191, People's Republic of China

⁴ Applied Chemistry Department, Tianjin University, Tianjin 300072, People's Republic of China

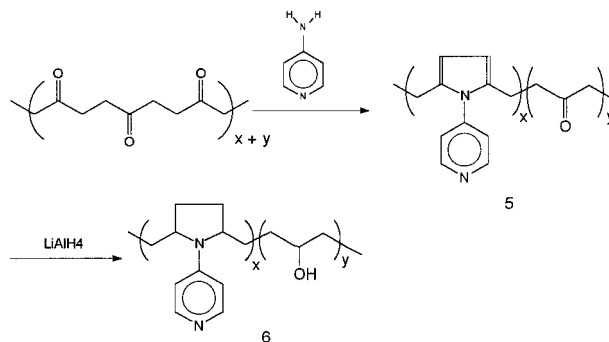
Received 1 December 1997; accepted 11 January 1998

INTRODUCTION

In 1967, Litvinenko and Kirichenko discovered that 4-(*N,N*-dimethylamino)pyridine (**1**, DMAP) could exercise a higher activity than that of pyridine over an acylation reaction when DMAP was used as a supernucleophilic catalyst.¹ Afterward, Steglich and Höfle proved that the catalytic capacity of 4-pyrrolidinopyridine (**2**, PPY) was higher than that of DMAP.² The reason for this result may due to the special structure of the five-membered ring in PPY. From then on, many researchers have sought to synthesize polymers which have this structure of PPY. For example, Narang and Ramharack³ performed a reaction involving 4-aminopyridine and maleic anhydride copolymers. The poly(4-*N*-pyrrolidinopyridine) copolymers (**3**) were obtained by reduction of the above copolymers. In 1985, Mathias et al. prepared homopolymers and copolymers that contain the PPY structure by involving the 4-(*N,N*-dialkylamino)pyridine (**4**, DAAP) in a cyclopolymerization with 2,2'-azobis(2-amidinopropane)hydrochloride as an initiator.⁴ DAAP polymers demonstrated a catalytic activity, which was even higher than that of PPY:

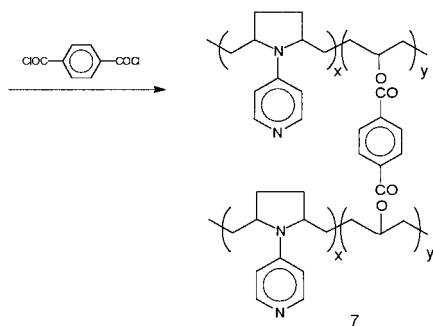


But the two separated double bonds in the DAAP monomer cannot enter into a cyclopolymerization reaction unless under the Butler conditions of reaction.⁵ In that case, the reaction time is rather long and many by-reactions may occur. The two separated double bonds tend to enter into copolymerization, respectively, with each of the other monomers to form crosslinked polymers, the structures of which are hard to control. Meanwhile, what remained crucial was to have the macromolecular backbone of the polymeric catalyst endowed with an appropriate degree of hydrophilicity and lipophilicity so as to increase the affinity between the catalysts and the reaction system. We have previously reported the synthesis of epoxide resin with alkylaminopyridine functions in order to overcome this problem.⁶ Unfortunately, there is no five-membered ring structure in the prepared resin:



Correspondence to: Y. Feng.

Journal of Applied Polymer Science, Vol. 69, 2303–2304 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/112303-02



In this article, we intended to synthesize a new kind of polymeric resin containing the PPY structure and hydroxyl groups. This meant bringing about a reaction involving 4-aminopyridine and polyketon, that is, alternating copolymer of carbon monoxide and ethylene. The final yield was a linear polymer containing the pyrrolediy structure and the remaining carbonyl groups. This reaction can be controlled by the degree of the reaction and the molar ratio of the amino groups and carbonyl groups, so that polymer **5** with x from 0.30 to 0.78 could be prepared by this method. Polymer **6** can be obtained by reduction of polymer **5** with AlLiH_4 . Then, a crosslinked polymer was effected by involving 1,4-dibenzene dicarbonyl dichloride; this gave a network structure **7**. This polymeric supernucleophilic reagent **7**, which was prepared according to the above simple method, possessed remarkable approachability and was capable of being repeatedly used.

EXPERIMENTAL

The 4-aminopyridine was supplied by Sigma Chemical Co., USA. An alternating ethylene-carbon monoxide copolymer (E-CO) was prepared according to the literature methods.⁷ As a means of representation, the FTIR of the Nicolet 5 DX Model was adopted for effecting the analysis of the functional groups. ¹H-NMR spectra were recorded on a Bruker AC-P 200 Model spectrometer. The C, H, and N analyses were achieved on an elemental analyzer: the PE-2400 Model. The ratio of the number of carbonyl groups reacted to the total number of carbonyl groups originally present, $2X/(2X + Y)$ [see polymer (5)], was determined from the element analyses.

Poly[ethylene-*N*-(*p*-pyridyl)pyrrolediy] (5)

A mixture of the E-CO copolymer (1.0 g) and 4-aminopyridine in 20 mL of chlorobenzene was allowed to reflux under N_2 for 24 h. The resultant mixture was centrifuged, and a brown polymer was precipitated by addition of the obtained solution to a mixture of diethyl ether and pentane. The product was washed with hot ethanol and diethyl ether and dried under a vacuum.

Yield: 0.90 g. ¹H-NMR (CDCl_3 , ppm): 8.2(d,2H), 6.8(d,2H), 5.7–5.9(m, 2H), 2.8(br, 7.5H), 2.3(br,4H). IR(KBr, cm^{-1}): 3082, 2920, 1710, 1690, 1605, 1580, 1520, 1400, 1030, 830.

ANAL: $(\text{C}_{11}\text{H}_{10}\text{N}_2)_x(\text{C}_3\text{H}_4\text{O})_y$. Found: C, 72.55%; H, 6.36%; N, 10.18%. Then, X , 0.32; Y , 0.60.

Hydrogenation of Polymer 5

A suspension containing 0.90 g of polymer **5** ($X = 0.32$, $Y = 0.60$) and 2.0 g LiAlH_4 in 50 mL THF was refluxed under N_2 for 4 h. Following the decomposition of residue LiAlH_4 by small amount of water, a light yellow polymer (**6**) was obtained by filtration and precipitation and then dried under a vacuum.⁸

Yield: 0.81 g. ¹H-NMR (CDCl_3 , ppm): 8.2(d,2H), 6.8(d,2H), 4.5(s,1.9H), 4.0(m,1.9H), 3.7(m,2H), 1.0–1.4(m, 16.5H), IR (neat, cm^{-1}): 3384, 3083, 2920, 1620, 1580, 1507, 1400, 1029, 830.

ANAL: Calcd for $(\text{C}_{11}\text{H}_{14}\text{N}_2)_{0.32}(\text{C}_3\text{H}_6\text{O})_{0.60}$: C, 70.56%; H, 8.93%; N, 9.90%. Found: C, 70.53%; H, 8.97%; N, 9.92%.

Crosslinked Polymer (7)

A solution of 1,4-benzene dicarbonyl dichloride (1 mmol) in 30 mL of CHCl_3 was added to the stirred solution of polymer **6** (0.81 g). The solution was stirred for 2 h at the refluxing temperature. The resultant yield was a solid matter. This solid matter underwent a process of extraction with methanol, THF, CHCl_3 , and CH_2Cl_2 . The extracted matter was dried under a vacuum.

Yield: 95% yellowish solid. IR(neat, cm^{-1}): 3384, 3080, 2925, 1760, 1603, 1585, 1509, 1400, 1213, 912, 844, 830.

REFERENCES

1. L. M. Litvinenko and A. I. Kirichenko, *Dokl. Nauk. SSSR Ser. Khim.*, **176**, 97 (1967).
2. W. Steglich and G. Höfle, *Angew. Chem. Int. Ed. Engl.*, **8**, 981 (1969).
3. S. C. Narang and R. Ramharack, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 147 (1985).
4. L. J. Mathias, R. A. Vaidya, and R. H. Bloodworth, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 289 (1985).
5. G. B. Butler, in *Polymeric Amines and Ammonium Salts*, E. J. Goethals, Ed., Pergamon, New York, 1979, pp. 125–142.
6. J. W. Sun, J. T. Huang, J. Q. Zhang, and S. H. Zheng, *J. Appl. Polym. Sci.*, **55**, 1865 (1995).
7. T. W. Lai and A. Sen, *Organometallics*, **3**, 866 (1984).
8. Y. K. Feng, J. W. Sun, F. L. Yao, Y. B. Yu, *J. Appl. Polym. Sci.*, **68**, 855 (1998).